

# ELECTROCHEMICAL CELL

## BACKGROUND OF THE INVENTION

### Field of the Invention

The invention relates to an electrochemical cell which is used in particular for the electrolysis of an aqueous solution of hydrogen chloride by a membrane process with a gas diffusion electrode functioning as the cathode.

### Description of Related Art

Aqueous solutions of hydrogen chloride, also referred to below as hydrochloric acid, are obtained as a by-product in many chemical processes, in particular, in processes in which organic hydrocarbon compounds are oxidized with the aid of chlorine. Many of these organic chlorine compounds are important intermediates for industrial chemistry, for example, in the production of plastics. The recovery of chlorine from these hydrochloric acids is of economic interest since the residual chlorine can be used, for example, to conduct further chlorinations. Chlorine from hydrochloric acid can be recovered, for example, electrolytically, that is, by electrolysis.

A process for the electrolysis of hydrochloric acid is disclosed, for example, in U.S. Patent No. 5,770,035, the content of which is incorporated herein by reference. In a typical process, an anode compartment with a suitable anode is employed that is made, for example, of a substrate of a titanium-palladium alloy coated with a mixed oxide of ruthenium, iridium and titanium. During use, the anode compartment is filled with an aqueous solution of hydrogen chloride. The chlorine formed at the anode escapes from the anode compartment and is fed to a suitable treatment. The anode compartment is generally separated from the cathode compartment by a commercial cation exchange membrane. A gas diffusion electrode rests on the cation exchange membrane on the cathode side. The gas diffusion electrode in turn rests on a current distributor. Gas diffusion electrodes are, for example, oxygen-consuming cathodes (OCC). When an OCC is employed as a gas diffusion electrode, an oxygen-containing gas or pure oxygen is usually passed into the cathode compartment and the oxygen reacts at the OCC.

The electrochemical formation of gas at the electrode adversely affects the electrolysis process. In addition to potentially negative hydrostatic and hydrodynamic effects, the gas bubbles that form result in an increased ohmic resistance in the electrolyte. In order to counteract the influences of the gas bubbles, DE-A 3 401 637 proposes an electrolysis process in an electrochemical cell with a separated anode compartment and cathode compartment, in which one or both electrodes have a passage, and an electrolyte flows from top to bottom through one or both half-cells so that the electrodes are wet. Thus, the electrolyte flows in a direction opposite to the direction the electrochemically formed gas is flowing. The resulting air bubbles burst at the phase boundary between the descending electrolyte film and the adjacent gas space.

### SUMMARY OF THE INVENTION

An object of the present invention was to provide an electrochemical cell for a membrane electrolysis process, which cell has, as the anode, a metal electrode preferably having as large an electrochemically active surface as possible, and orifices that make it possible to conduct gas formed from the side facing the cathode into a space located behind the metal electrode. In particular, the electrochemical cell is suitable for use in the electrolysis of an aqueous solution of hydrogen chloride, the cathode used typically being a gas diffusion electrode. The anode compartment is preferably completely filled with the hydrochloric acid, the latter flowing through the anode compartment from bottom to top.

These and other objects can be achieved, for example, by providing one or more orifices of the metal electrode with a guide structures which conduct the gas formed into the space behind the metal electrode. At the same time, the metal electrode is preferably angled and/or curved, with the result that its electrochemically active area is increased. The present invention is further directed to electrodes as well as to methods for their use.

Additional objects, features and advantages of the invention will be set forth in the description which follows, and in part, will be obvious from the description, or may be learned by practice of the invention. The objects, features and advantages of the invention may be realized and obtained by means of the instrumentalities and combination particularly pointed out in the appended claims.

## BRIEF DESCRIPTION OF THE DRAWINGS

The invention is explained in more detail below with the aid of preferred embodiments with reference to the attached drawings.

FIG. 1 shows a diagram of a first preferred embodiment of the electrode structure in perspective view

FIG. 2 shows a diagram of a second preferred embodiment of the electrode structure in perspective view

FIG. 3 shows a diagram of a third preferred embodiment of the electrode structure in perspective view

FIG. 4 shows a diagram of a fourth preferred embodiment of the electrode structure in perspective view

FIG. 4a shows a section of the embodiment shown in FIG. 4

FIG. 5 shows a diagram of a fifth preferred embodiment of the electrode structure in perspective view

## DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

The invention generally relates to an electrochemical cell suitable for a membrane electrolysis process, comprising at least one anode compartment having a metal electrode as the anode, a cathode compartment having a gas diffusion electrode as the cathode and an ion exchange membrane arranged between the anode compartment and cathode compartment. The metal electrode is generally capable of being dipped into an electrolyte and is provided with orifices for the passage of the gas formed during operation and is further optionally angled and/or curved, for example as shown in Figures 1-5. The orifices are preferably provided with one or more guide structures which are capable of conducting gas formed onto the side of the metal electrode facing

away from the cathode.

The orifices of the electrode can comprise slots or holes and/or can optionally be formed by the meshes of an expanded metal. In order to conduct the gas in a controlled manner into the space behind the metal electrode, (also referred to herein as the "back space"), the guide structures at the orifices are advantageously inclined in the direction of the ion exchange membrane. Thus, the gas that builds up at the surface of the metal electrode facing the ion exchange membrane is conducted away from the surface and, on ascending, is discharged from a narrow gap between the metal electrode and the ion exchange membrane. This prevents the gas from collecting in the narrow intermediate space and substantially minimizes the likelihood of increased resistance in the electrolyte.

In a preferred embodiment of the electrochemical cell according to the invention, the orifices of the metal electrode advantageously have a total cross-sectional area which is in the range from 20% to 70% of the area which is formed by the height and width of the metal electrode. In the case of a perpendicular arrangement of the metal electrode in the electrochemical cell, the length of the substantially perpendicularly arranged side of the electrode is to be regarded as the "height" of the metal electrode, while the length of that side of the electrode which is arranged substantially parallel to the opposite electrode and horizontally is to be regarded as the "width."

If the electrode substantially comprises a metal sheet, the electrode is preferably not flat but rather, is advantageously curved and/or corrugated. For such an electrode structure, a corrugated, zigzag-shaped or rectangular cross section is preferably chosen. In this way, the size of the electrochemically active surface of the metal electrode is increased. In particular, such an electrode structure is important for the electrolysis of aqueous solutions of hydrogen chloride (hydrochloric acid) since, owing to the relatively high conductivity of hydrochloric acid, an electrochemical reaction is effected, even when there is a relatively large distance between the electrode and the opposite electrode. The electrochemically active surface of the metal electrode is formed in particular by that surface of the metal electrode facing the opposite electrode, in this case the cathode. However, an electrochemical reaction also occurs at surfaces that do not face the opposite electrode. This applies, for example, to surfaces at right angles to the opposite

electrode, such as, for example, edges, or surfaces facing away from the opposite electrode, such as, for example, the back of the metal electrode. The "electrochemically active surface" is therefore to be understood as meaning the proportion of the total surface area of the metal electrode at which an electrochemical reaction takes place. In some embodiments of the present invention, the ratio of electrochemically active surface area to the surface area which is formed by the height and width of the metal electrode is preferably at least 1.2.

In a further preferred embodiment of the electrolysis cell, the metal electrode preferably has a depth of at least 1 mm. The depth is regarded as the side length of the metal electrode which is arranged substantially perpendicular to the opposite electrode and horizontally. In the case of a corrugated cross section of the metal electrode, the depth preferably corresponds to twice the amplitude of the wave. Expressed otherwise, the depth corresponds to the difference between the minimum and maximum distance formed by one of the edges of the electrode and of the ion exchange membrane. The same preferably applies to the depth in the case of a zigzag-shaped cross section of the electrode.

With a suitable mesh size, web thickness and web width, the expanded metal, if employed, preferably also has the same desired properties as the electrode structure, namely a large electrochemically active surface which has depth, and orifices for conducting away the gas. The mesh structure enables the gas to be conducted away to the back of the metal electrode. In such a case, the webs perform the function of the guide structure if the expanded metal is arranged so that the webs are inclined in the direction of the opposite electrode. It is also possible to use a combination of two or more identical or different expanded metals if at least one of the expanded metals is installed in the electrochemical cell as a metal electrode, in particular as the anode, in the manner described. The metal electrode is preferably based on two adjacent expanded metals, the expanded metal facing the opposite electrode preferably having a finer structure than the expanded metal facing away from the opposite electrode. Moreover, the more finely structured expanded metal is preferably rolled flat while the webs of the more coarsely structured expanded metal preferably serve as guide structures and is advantageously arranged in such a way that the mesh webs are inclined in the direction of the opposite electrode.

A typical cell according to the invention can be used in any desired application and in particular for the electrolysis of aqueous solutions of hydrogen chloride. The anode half-cell generally has an inlet and an outlet for the electrolyte, which flows from bottom to top through the half-cell and completely fills it. The outlet of the electrolyte simultaneously typically serves as an outlet for the gas formed. A suitable anode is, for example, a noble metal-coated or noble metal-doped titanium electrode. Suitable anodes include a titanium electrode or titanium alloy electrode, in particular a titanium-palladium alloy electrode which is provided with an acid-resistant, chlorine-evolving coating, for example based on a ruthenium-titanium mixed oxide, or on an iridium oxide or based on platinum. The anode half-cell is typically separated from the cathode half-cell by an ion exchange membrane. A gap is generally present between the anode and the ion exchange membrane. In particular, a gas diffusion electrode which functions as an oxygen-consuming cathode serves as the cathode. The gas diffusion electrode rests both against the ion exchange membrane and also against a current collector. If the gas diffusion electrode is used as an oxygen-consuming cathode, oxygen or an oxygen-containing gas can flow through the cathode compartment. It is also conceivable to influence the oxygen inside the cathode compartment in its direction of flow using baffles or other similar devices. The oxygen can be passed in from below via an inlet and removed again at the top via an outlet. However, it is also possible for the oxygen to flow from top to bottom or for there to be lateral flow in the cathode compartment in any desired direction, for example, from bottom left to top right and so on. With respect to the reaction taking place, oxygen should preferably be supplied in a superstoichiometric amount in order to achieve advantageous results in some applications.

Gas diffusion electrodes which contain a catalyst of the platinum group, preferably platinum or rhodium, are preferably used. Gas diffusion electrodes from E-TEK (USA) which have 30% by weight of platinum on active carbon with a noble metal coating of 1.2 mg of Pt/cm<sup>2</sup> on the electrode may be mentioned as exemplary suitable electrodes by way of example.

Suitable ion exchange membranes include, for example, those comprising perfluoroethylene which contain sulfo groups as active centres. For example, commercial membranes from DuPont can be used, for example the membrane Nafion®

324. Single-layer membranes having sulpho groups of identical equivalent weights on both sides as well as membranes having sulpho groups with different equivalent weights on both sides are suitable. Membranes having carboxyl groups can also conceivably be used. Any desired ion exchange membrane can be employed depending on the intended application.

The current distributor on the cathode side may comprise, for example, expanded titanium metal or noble metal-coated titanium. It is also possible to use alternative stable materials as well as any other desired current distributor available to those of skill in the art.

In the embodiment described below, the surface of a metal electrode which faces an ion exchange membrane and hence the opposite electrode is referred to as the "front", and accordingly the surface facing away from the ion exchange membrane is referred to as the "back". In a typical electrochemical cell according to the present invention, the electrode is preferably not located on the ion exchange membrane, but rather, a gap filled with electrolyte is present between the anode and ion exchange membrane. In such a case, the gap is preferably not separated from the remaining space of the half-cell. The gap can advantageously be, as a rule from about 1 to 3 mm. It is formed by virtue of the fact that the anode compartment is preferably kept at a higher pressure than the cathode compartment. Thus, the ion exchange membrane is pressed onto the gas diffusion electrode and then in turn, onto a current collector. It is preferable that the cell is arranged such that a suitable electrolyte preferably can flow freely from bottom to top through the half-cell. The space of the half-cell which is adjacent to the back of the electrode is also referred to herein as "back space".

In the embodiment shown in FIG. 1, the electrode includes perpendicularly arranged metal lamellae 10 which are substantially at right angles to the ion exchange membrane. Baffle plates 12 which are advantageously inclined in the direction of the ion exchange membrane are present as guide structures in each case between two adjacent lamellae. The baffle plates 12 aid ascending gas being conducted from the front of the electrode, *i.e.* the side facing the ion exchange membrane, backwards into the back space of the electrochemical half-cell through the orifices 14. Contact of the lamellae can be effected, for example, via current feeds 16. The depth of the lamellae is preferably in the

range from about 1 to 40 mm and the distance between two adjacent lamellae is preferably in the range from about 1 to 10 mm.

In a further preferred embodiment (not shown here) which is similar to the principle according to that shown in FIG 1, the perpendicularly arranged lamellae are at an angle of from 50 to 90° to the ion exchange membrane.

In the embodiment shown in FIG 2, the structure of the electrode 20 and of the baffle plates corresponds substantially to the embodiment shown in FIG. 1 (identical or different components are therefore denoted by the same reference numerals). The substantial difference is that the lamellae 20 are connected at their edges facing away from the ion exchange membrane to a metal sheet 28 which has, below the baffle plates 22, orifices 24 for conducting away the gas. The metal sheet 28 mounted to the back of the lamellae is thus substantially parallel to the ion exchange membrane.

In an embodiment shown in FIG. 3, the metal electrode 30 is based on a corrugated cross section. The orifices 34 are present in the region of the wave summits facing away from the ion exchange membrane. The guide structures 32 are preferably formed of metal sheets which are substantially the shape of a half-wave and are mounted above the orifices 34 and inclined in the direction of the ion exchange membrane. Such an electrode structure can be produced in a simple manner, for example, by punching substantially triangular orifices 34 in the region of the wave summits from the back of the electrode 30. The triangular orifices are preferably not punched out completely, but the punched parts each remain connected to the electrode in the region of the upper vertex of the triangle, so that the punched parts can be bent as guide structures 32 in the direction of the ion exchange membrane and can be arranged at an angle of inclination of preferably from 10 to 60°. The guide structures 32 can optionally be welded at their lateral edges to the electrode 30. Preferably, however, orifices 34 are punched from the back of the electrode 30 in a shape corresponding to the shape of the wave summit, since in this way the guide structures 32 bent towards the front of the electrode 30 and inclined in the direction of the opposite electrode, terminate with the electrode. An additional connection of the guide structures 32 to the electrode 30 can therefore be eliminated. In such a method of production, the area of the punched orifices 34 substantially determines the area of the guide structures 32. Those punched metal parts of the electrode which



function as guide structures can also be reduced in size so that they project to a lesser extent into the space between electrode and ion exchange membrane. Preferably, the size of the orifices 34 is chosen so that the area of the guide structures 32 is close to the same as, or is exactly the same as the area of the wave summit. The depth of the electrode, which is understood here as meaning the distance from wave summit to wave valley, *i.e.* double the amplitude of a wave, is preferably from 2 to 40 mm. The distance between two adjacent wave summits or valleys, which would correspond to the wavelength, is preferably from about 3 to 30 mm. In this embodiment, the gas generally flows substantially in the direction marked with the arrow 39.

A further embodiment (not shown here) is in principle an electrode structure similar to that shown in FIG. 3, but the electrode is based on a zigzag-shaped cross section. Analogously to the method of production described above, this electrode structure can be produced, for example, by punching out a triangular orifice from behind in the region of the vertices facing away from the ion exchange membrane.

The embodiment shown in FIG. 4 differs from that shown in FIG. 3 once again only in the cross section on which the electrode structure 40 is based. Here, it is a rectangular cross section, the orifices 44 (FIG. 4a) being present on the longitudinal sides face away from the ion exchange membrane. These are preferably arranged substantially parallel to the ion exchange membrane. The guide structures 42 conduct the gas into the back space of the half-cell, preferably corresponding to the direction marked with the arrow 49 (FIG. 4a).

In a further preferred embodiment (FIG. 5), with a likewise rectangular cross section of the electrode structure 50, the orifices 54 are arranged not on the rear longitudinal side, but rather, on one of the transverse sides, *i.e.*, on one of those sides of the electrode which are perpendicular to the ion exchange membrane. In this embodiment, the guide structures 52 are accordingly not inclined in the direction of the ion exchange membrane but instead, in the direction of the opposite transverse side of the electrode. The gas flow from the front to the back of the electrode is marked with the arrows 59.

An electrode structure having a large electrochemically active surface and orifices with guide structures for conducting the gas into the back space of the half-cell can also comprise expanded metals if desired. Thus, a further preferred embodiment includes at least two expanded metals adjacent to one another, the expanded metal facing the ion exchange membrane particularly preferably having a finer structure than the expanded metal facing away from the ion exchange membrane. A more finely structured expanded metal is characterized by a smaller mesh width and mesh size and a smaller web width and web thickness than a more coarsely structured expanded metal. Moreover, the more finely structured expanded metal is preferably rolled flat and the more coarsely structured expanded metal is not arranged arbitrarily, but rather, is preferably arranged in such a way that the mesh webs perform the function of guide structures. The meshes are preferably rhombic or square and the webs of the coarser expanded metal facing away from the ion exchange membrane are typically inclined in the direction of the ion exchange membrane. The total area of the orifices, both in the case of the more finely structured and in the case of the more coarsely structured expanded metal, are preferably in the range from 20 to 70% of the area which is given by the external dimensions, *i.e.* the edge lengths, of the expanded metals.

The following parameters are used for characterizing the expanded metals: the web thickness corresponds to the thickness of the metal sheet used for the production of the expanded metal. The web width results from the distance between two cuts parallel to one another but offset. The mesh size characterizes the length of the cut, and the mesh width characterizes the maximum distance between two adjacent webs as a result of stretching deformation.

Surprisingly, it has been found that, in this preferred embodiment of the invention, a lower operating voltage is employed as compared with the operating voltage in electrolysis cells having conventional electrode structures. This voltage effect is clearly evident in the examples described below.

### Examples

The electrolysis of an aqueous solution of hydrogen chloride (hydrochloric acid) was carried out using a gas diffusion electrode as an oxygen-consuming cathode. The concentration of the hydrochloric acid was 13% by weight and its temperature on entry

into the anode half-cell was adjusted so that the temperature in the discharge was 60°C. The circulation volume flow of the hydrochloric acid was adjusted so that the flow rate of the hydrochloric acid in the anode half-cell was 0.3 cm/s. The material of the anodes was a titanium-palladium alloy activated with a ruthenium-titanium mixed oxide layer (DSA® coating). A cationic membrane from DuPont, Nafion® 324 type was used between the anode compartment and the cathode compartment. The cathode used was a gas diffusion electrode from E-TEK (USA), which was based on carbon and activated with rhodium sulphide. The gas diffusion electrode was fastened to the current collector, and was formed of an activated titanium-palladium expanded metal. The width of the electrode was 730 mm and the height was 1200 mm. The minimum distance between the anode and the cation exchange membrane was 3.5 mm.

#### **Example 1**

The anode used as a combination of two titanium expanded metals adjacent to one another, a more finely structured expanded metal being applied to a more coarsely structured expanded metal. The more finely structured expanded metal had a mesh size of 4.2 mm and a mesh width of 3.1 mm and a web width of 0.6 mm and a web thickness of 0.4 mm. Accordingly, the total area of the orifices was 53% of the area of the expanded metal. This expanded metal was rolled flat to a thickness of 0.5 mm. The more coarsely structured of the two expanded metals had a mesh size of 13.2 mm, a mesh width of 6.3 mm, a web width of 2.4 mm and a web thickness of 3.5 mm. Thus, the total area of the orifices was 24% of the area of the expanded metal. The anode was installed in such a way that the finer expanded metal which had been rolled flat faced the cation exchange membrane.

The voltage was 1.59 V at a current density of 5 kA/m<sup>2</sup>.

#### **Example 2 (comparative example)**

The anode comprised a single coarsely structured expanded metal having a mesh size of 6.2 mm, a mesh width of 3.6 mm and a web width of 1.1 mm and a web thickness of 1 mm. The total area of the orifices was accordingly 24% of the total area of the anode.

The voltage was 1.67 V at a current density of 5 kA/m<sup>2</sup> and was thus higher than in the electrolysis of a hydrochloric acid solution under comparable conditions but with the special combination of a more finely structured expanded metal which had been rolled flat and faced the cathode and a more coarsely structured expanded metal located behind.

According to certain embodiments of the present invention, it is possible to conduct electrolysis of hydrogen chloride at voltages less than 1.67 V at a current density of 5 kA/m<sup>2</sup>. The voltage will also be reduced at other current densities.

Additional advantages, features and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative devices, shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.

All documents referred to herein are specifically incorporated herein by reference in their entireties.

As used herein and in the following claims, articles such as "the", "a" and "an" can connote the singular or plural.

The priority document, German Patent Application No. 102 34 806.5 filed July 31, 2002 is incorporated herein by reference in its entirety.